The role of exciplex states in phosphorescent OLEDs with poly(vinylcarbazole) (PVK) host

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Abstract

Polymer light emitting diodes (PLEDs) may revolutionize lighting and display industries. PLEDs would enable printing of display or lighting panels on large area substrates that could substantially reduce fabrication costs by avoiding expensive vacuum processes presently used in OLED technologies. PVK is one of the most popular hosts for blue PLEDs. However, PVK has very poor electron transport properties and oxadiazole based electron dopants, e.g. PBD or OXD-7, are used to improve charge transport. This is generally ascribed to capture and transport of electrons on the PBD or OXD-7. Here we show that this is not necessarily the only reason for improved efficiency upon PVK doping. We demonstrate that devices with PVK doped with PBD or OXD-7 have emission lasting up to 1 ms which in some cases may be greater than prompt emission from excitons formed initially on the dopant. This long-lived emission is arising mainly due to formation of an exciplex between the PVK and PBD / OXD-7. This exciplex state then repopulates dopant iridium complexes over a long period of

time giving very long-lived emission. We also note, that this exciplex-fed long-lived emission from heavy metal complexes is observed in several PLEDs with PBD and PVK (and also OXD-7) doped with blue or green iridium phosphors indicating this to be a general phenomenon.

Manuscript text

1. Introduction

Since the discovery of polymer light emitting diodes (PLEDs)[1] it has been assumed that singlet and triplet excitons are formed in the ratio of 1:3 which fundamentally limits external quantum efficiency of PLED devices. This is due to the fact that 75% of excitons formed are triplet states which are weakly emissive[2] and it is clear that one could increase the quantum efficiency of PLEDs four-fold by utilization of triplet excitons. This has been successfully achieved using heavy metal complexes as emissive dopants where phosphorescence efficiency is increased due to (heavy metal enhanced) spin-orbit coupling.[3,4] In order to avoid concentration quenching, heavy metal complexes are doped into various polymer hosts, poly(vinylcarbazole) (PVK)[5,6] being one of the most popular, due to its high triplet level suitable for green dopants[7]. It has been reported that green PLEDs with a PVK host can achieve up to 40 cd/A efficiency[6]. Because PVK has very poor electron transporting and injection properties doping electron transport materials such as 2,2'-(1,3-phenylene)bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole] (OXD-7) or 2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) into the PVK host improves efficiency.[8] This is generally ascribed to capture and transport of electrons on the PBD or OXD-7 because the LUMO level of PBD

at 2.4 eV is close to the Ba work function at 2.7 eV, and also because PBD is an efficient electron transport material.[9]

In this paper, we show that this improvement in device efficiency cannot be wholly attributed to the improved electron injection and transport properties, but should also be attributed to long-lived emission from iridium dopants lasting up to milliseconds, which is much longer than the lifetime of the pure iridium complex which is in the range of microseconds[10]. We suggest possible origins of this long-lived emission in PLED devices and show that it contributes to more than *half of the total emission* in some cases. An exciplex formed between PVK and PBD and a charge transfer state between the iridium complex and the PVK contribute to this emission. It is estimated, that the former contribution is greater. We emphasize that this is a general observation for many iridium based dopants in PVK where OXD-7 or PBD are used, as we observe this long-lived emission in PLEDs with various emitters, including di-iridium complex **1**[11], the blue emitter (iridium(III)bis[2-(2,4-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato-N,$C^{2'}$]picolinate) **2**, and the green emitters *fac*-tris(2-phenylpyridine)-iridium **3** and *fac*-tris[2-(2-pyridinyl-kN)(5-(3,4-bis(2-methylpropyloxy)phenyl) phenyl)-kC]-iridium(III) **4** (Figure 1). Complex **4** was chosen as it is a more soluble analogue of **3**. We concentrate on di-iridium emitter **1** and PBD, where the long-lived delayed emission in **1**[11] provided maximum contribution to the overall device emission, whereas the data for the other emitters **2-4** is provided in supplementary information.

2. Experimental

2.1 Device Fabrication

Polymer light emitting devices (PLED) are fabricated on indium tin oxide (ITO)-coated glass substrates of thickness 125 nm and possessing a sheet resistance of 15 Ω /□. Poly(3,4-ethylenedioxythiophene) doped with high work function hole injection layer poly(styrenesulfonic acid) (PEDOT:PSS) (HIL1.5), from CLEVIOS^{TM}, is spin coated at 2500 rpm for 60 sec to produce a ~50 nm thick hole-injecting / transporting layer (HTL). The PEDOT:PSS layer is annealed at 200 ^{o}C for 5 min to remove any residual water. A chlorobenzene solution of 22 mg / ml of PVK is doped with 50% w/w of 2,2'-(1,3-phenylene)bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole] (OXD-7) or 40% w/w 2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD). Blended devices were made by mixing 5% or 8% w/w of the Ir complexes. The prepared mixtures were filtered with a 0.45 μm pore filter and spin coated at 2500 rpm for 1 min on the top of the PEDOT:PSS layer and baked for 10 min at 120 °C. Each sample was shadow masked to produce four identical devices of area 4x5 mm; the samples were then introduced into a nitrogen glove box, where 4 nm barium cathodes were evaporated onto the device at a rate of ~ 1 Å/s under vacuum at a pressure of ca. 1x10^{-6} torr. This was followed by the deposition of a 100 nm capping layer of aluminium under the same evaporation conditions. Therefore, the device configuration for all complexes was ITO/PEDOT:PSS (50 nm)/PVK:OXD-7 or PBD:Ir-Complex (100±10 nm)/Ba(4 nm)/Al(100 nm). All samples are encapsulated inside a glove box using DELO UV cured epoxy (KATIOBOND) and capped with a 1.2x1.2 cm microscope glass slide then exposed to UV light for 3 min. Current-voltage data, device efficiency, brightness and electroluminescence spectra were measured in a calibrated Labsphere LMS-100 integrating sphere. A home written NI LabVIEW programme was used to control an Agilent 6632B DC power supply, and the emission properties of the device were measured using an Ocean Optics USB4000 CCD fibre optic spectrometer. Thicknesses of the various layers in the

device were measured with a J A Woolam VASE Ellipsometer using thin films which had been spin coated on Si/SiO_2 substrates under the same conditions as the device films.

2.2 EL and PL transients

PL transients were recorded by exciting films at 355 nm with 150 ps length YAG laser (EKSPLA) pulses and collecting light using a JobinYvon spectrograph and gated iCCD camera (Stanford Computer Optics) by exponentially increasing delayed and integration times as described in ref[17]. This allows to record up to 10 orders of magnitude in time and intensity of the PL decay.[18] For EL transients the same light collection setup and data collection methods were employed and as excitation source an HP 8114A pulse generator was used (length 1 ms).

3. Results and Discussions

Four types of PLEDs were fabricated with structures: ITO/PEDOT-PSS/PVK:40% PBD: 5% **1**/Ba/Al (type 1), ITO/PEDOT-PSS/PVK:40% PBD/Ba/Al (type 2), ITO/PEDOT-PSS/PVK/Ba/Al (type 3), ITO/PEDOT-PSS/PVK: 5% **1**/Ba/Al (type 4). Complex **1** is a very efficient green di-iridium complex that we have reported recently[11]. The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are depicted in Figure 1.[11] In these devices electrons are transported via PBD molecules and holes via PVK chains and most of the excitons should be created on the Ir dopant as its LUMO and HOMO levels should trap electrons and holes from the PBD and PVK, respectively. However, it is also possible that exciplexes can be formed between the LUMO of PBD and the HOMO of PVK, which is confirmed by the observation of exciplex emission in

PVK:PBD devices without a phosphorescent dopant[12]. Exciplexes could be formed even when a dopant is present, as the latter is normally used at low concentrations in the range of 10%, whereas PBD is normally doped at 40% wt% ratio to PVK. When an iridium complex is doped into the emissive layer, the device emission will be dominated by the efficient complex emission as usually the exciplex has low radiative efficiency. Throughout this paper we will argue that the major part of the observed long-lived emission arises from exciplexes having triplet character which feed back to the Ir complex; we also show that their existence is crucial to the high efficiency of the devices under investigation.

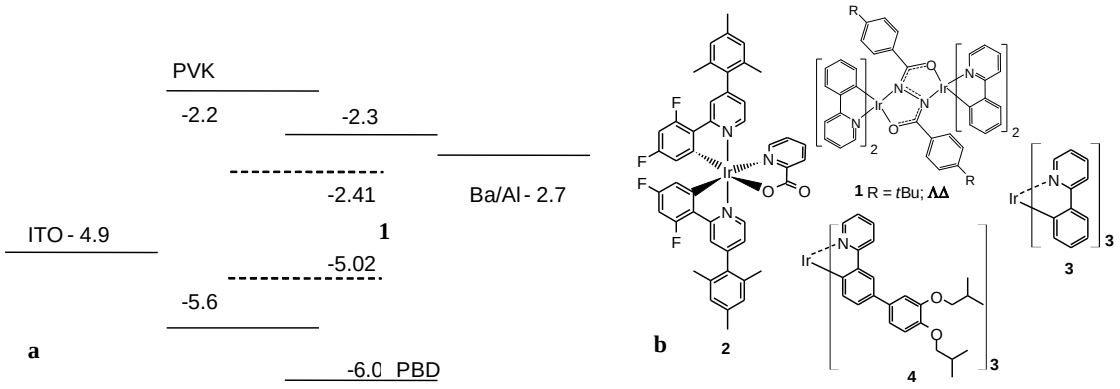

Figure 1. ***a****. HOMO (<-5 eV) and LUMO (>-2.41 eV) level diagram (in eV) of materials under investigation. Work functions of ITO and Ba/Al in eV are also provided. For* **1** the *HOMO level is taken from electrochemistry (vs ferrocene)[11]and the LUMO is calculated by subtracting the optical bandgap. PBD and PVK levels taken from[13] page 224.* ***b****. Chemical structures of complexes under investigation:* ***1*** *di-iridium complex reported in [11],* ***2*** *iridium(III)bis[2-(2,4-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato-N,C$^{2'}$]picolinate),* ***3*** *-fac-tris(2-phenylpyridine)-iridium,* ***4*** *fac-tris[2-(2-pyridinyl-kN)(5-(3,4-bis(2-methylpropyloxy)phenyl) phenyl)-kC]-iridium(III)*

The electroluminescence (EL) and photoluminescence (PL) transients of these devices are shown in Figure 2. The EL transient was recorded at 14 V and 1 ms length pulsed excitation.

The EL transient curve of type 1 devices consists of two features on a log-log scale. A clear early time exponential decay is observed and at longer times there is a second linear feature with a power law dependence with the slope approaching -0.7. The emission spectra from both regions are, however, the same (Figure 2b.) The intensity contribution (calculated as the area under the region) of the power law part is ~65% of the total emission (*two times greater* than the exponential part). This is substantial and shows that the power law emission makes a very important contribution to the device efficiency. The PL transient with λ_{ex}=355 nm of the same device also shows the exponential and power law features with the slope of -0.6, however, with the major difference that now the power law contribution is considerably smaller (35% of the total emission). The power law contribution decreases even more (3% of the total emission) in the PL transient with λ_{ex}=450 nm. With λ_{ex}=450 nm the iridium complex is excited directly, as neither PBD nor PVK absorbs at this wavelength and concomitantly no PBD:PVK exciplex excited states are formed; hence clearly the greatest part of the long-lived tail contribution arises due to the presence of excited PVK and PBD species. Note, an exciplex has no stable ground state and so there can be no energy transfer to an exciplex state.

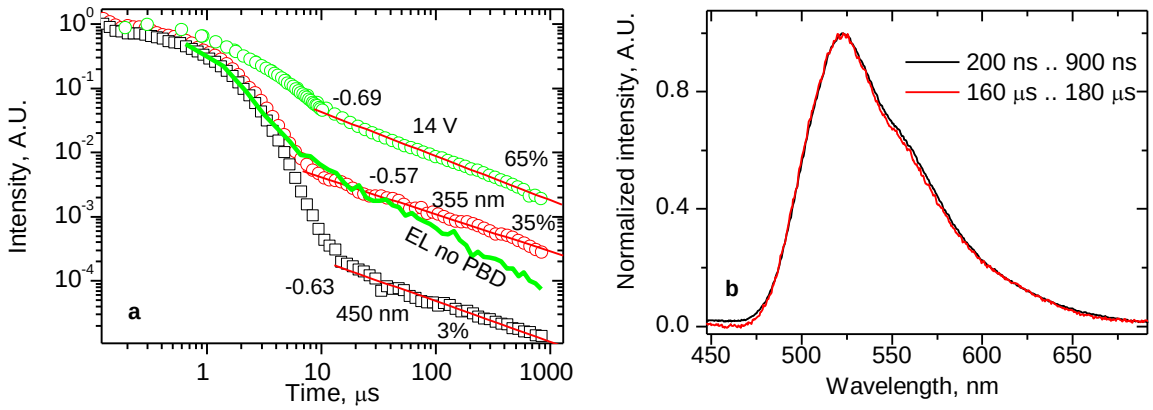

Figure 2. ***a****. Normalized EL and PL transients of ITO/PEDOT-PSS/PVK: 40% PBD: 5%* ***1****/Ba/Al device when exciting with 14 V 1 ms square pulse and with pulsed laser at 355 nm or 450 nm. Percentages indicated are contributions of power law intensity to the total emission (integration under the curve). Negative numbers are slopes of power law. EL of device without PBD (PVK: 5%* ***1****) added for comparison (green line).* ***b****. Time resolved spectra from ITO/PEDOT-PSS/PVK: 40% PBD: 5%* ***1****/Ba/Al device when exciting with 14 V 1 ms square pulse at exponential (black) and power law (red) decay regions, intensity normalized at peak.*

If PBD is not present in the device (Type 4) this power law contribution in the EL transient also decreases to 26% of the total emission value (Figure 3). This implies that the presence of PBD substantially increases the intensity of this long-lived emission. The power law component is not observed for the Type 3 device where PVK is an active layer. A similar type of long-lived power law emission in polymer films doped with an iridium complex has been observed previously by Rothe *et al;*[14]however, its contribution to the overall emission was negligible. Rothe *et al*[14] proposed that this emission arises from a charge transfer state between the complex and the PVK. It was suggested that this state is formed from the initially excited iridium complex ^{3}MLCT state due to a charge transfer from the ligand of the complex to a nearby host polymer site and subsequent return back to the iridium complex.

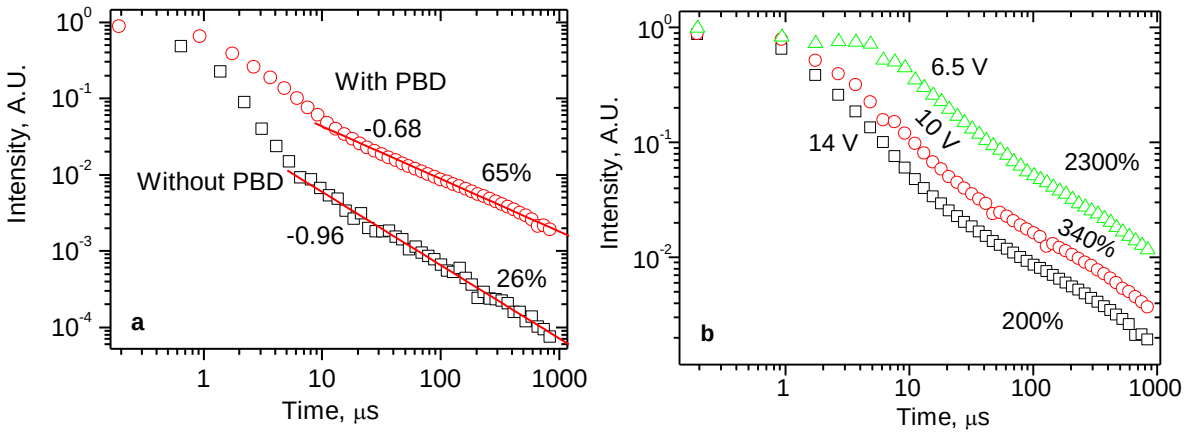

Figure 3. ***a****. EL transients of ITO/PEDOT-PSS/PVK: 40% PBD: 5%* ***1****/Ba/Al device and ITO/PEDOT-PSS/PVK: 5%* ***1****/Ba/Al when exciting with 14 V 1 ms square pulse. Percentages indicated are contributions of power law*

intensity to the total intensity. Negative numbers are slopes of the power law. ***b****. EL transients of ITO/PEDOT-PSS/PVK: 40% PBD: 5%* ***1****/Ba/Al device when exciting with 1 ms square pulse at various voltages. Percentages indicated are contributions of power law intensity versus exponential intensity.*

We observe similar behaviour of this long-lived feature as in the work of Rothe *et al*.[14]. Firstly, time resolved spectra from both the exponential part and the power law part of the curve are exactly the same. This means that emission is coming from the dopant at all times; however, it is unlikely that the power law emission is coming from excitons formed as a result of recombination on the dopant due to the short radiative lifetime of the dopant (in the range of 1 to 2 μs,[10, 11, 15] whereas the power law feature lasts up to milliseconds). We can also discount the hypothesis that the dopant, at late times, is fed from either PBD or PVK triplet states, as it is very unlikely that triplets formed on the PVK and PBD molecules have a lifetime in the range of milliseconds at room temperature (Figure 4). In recent studies on triplet dynamics in polymer and small molecule films it was shown that triplet lifetimes at room temperature are in the range of microseconds rather than milliseconds, which is 3 order of magnitude lower.[16-18] In addition, an iridium complex acts as a deep electron trap (Fig. 1) and it is likely that triplet excitons are not formed at all on PVK or PBD in devices, as PVK and PBD molecules are the least likely recombination centres. It is more likely that exciplex states between the HOMO of PVK and the LUMO of PBD will be formed (see Figure 1a for a HOMO-LUMO diagram). Furthermore, in agreement with Rothe *et al*,[14] we have observed that at higher voltage the emission is quenched with a power law decay (Fig. 3), while it does not impact on the exponential feature to such an extent. This also indicates that the origin of this emission is not an iridium ^{3}MLCT state, but instead a state having much more charge transfer character. It also rules out the possibility of enhanced triplet exciton formation from excitons created on either PVK or PBD via a long range resonantly enhanced heavy atom

effect [19]. Thus, it is possible that the long-lived emission (or at least part of it) in our devices arises because of the same reason as suggested by Rothe *et al.*[14]

Nevertheless, a mechanism must be found by which the long-lived emission contributes ~7-8 orders of magnitude more light to the total emission than that observed by Rothe *et al*.[14] Hence we propose that the dopant, at long times, is fed via exciton transfer from the long-lived exciplex state having triplet character, formed between PVK and PBD. This is supported by the existence of long-lived exciplex states in Type 2 devices with a PVK:PBD active layer (without a dopant), the lifetime of which is very similar to the lifetime of the long-lived power law region in Type 1 devices. Time resolved EL spectra of Type 2 device with PVK:PBD and Type 3 device with PVK-only active layers at early times (exponential decay region) and late times (power law region) are displayed in Figure 4. Devices with a PVK-only active layer emit at 410 nm, which can be ascribed to a mix of PVK singlet and PVK excimer emission,[20] whereas time resolved EL spectra of devices with PVK:PBD peak at 437 nm; this emission can be ascribed to the exciplex formed between the HOMO of PVK and the LUMO of PBD. Interestingly, we observe exciplex emission in Type 2 devices up to 1 ms, which we ascribe to emission from the exciplex triplet state. In addition, at very late times, emission centred at 530 nm is observed, which could be ascribed to PVK triplet dimer emission.[7] The exciplex triplet level should be close to that of the singlet level, as predicted by Beens *et al*[21] and experimentally shown by Frederichs *et al*.[22] This is the consequence of the small HOMO-LUMO overlap in exciplexes which reduces the singlet-triplet splitting (exchange energy).[23] Consequentially it is very difficult to distinguish between singlet and triplet spectra, hence we ascribe emission in PVK:PBD devices recorded at late times at ~437 nm to a PVK:PBD exciplex triplet by virtue of the long lifetime (in the range of hundreds of μs) in line with other recent results[24]. We thus propose that the

PVK:PBD exciplex with triplet character feeds the iridium complexes via exciton transfer, in line with the large increase (Figure 3) of long-lived emission when PBD is added to the device. This rationale also agrees with the observation that when we excite only the iridium complex in Type 1 devices, at 450 nm, very little long-lived emission is observed (Figure 2; PVK and PBD do not absorb at this wavelength) as few exciplexes are formed and only the mechanism suggested by Rothe *et al*[14]is present. This can be contrasted with the PL decay of the same Type 1 device at 355 nm excitation when PVK and PBD are also excited and long-lived emission increases substantially. Furthermore, after electrical excitation, when many more triplet states are formed (25% singlet and 75% triplet[25]) long-lived complex emission fed via the exciplexes increases to more than half of the total emission.

We observe 26% of long lived emission contribution in type 4 devices (with **1** and PVK). Subtracting this contribution from type 1 device (with PVK, PBD and **1**) long lived contribution of 65%, gives us 39%. In addition to, from PL measurements of device 1 (figure 2a, excited with 355%) we get 35% long lived emission contribution. This could imply that around 35-39% long lived contribution in device 1 comes from PVK and PBD exciplex, and the remaining 25% arising from charge transfer state between the complex **1** and the PVK[14]. However, we think this is just a coincidence and that this calculation can only give the lower limit of PBD and PVK exciplex contribution. Addition of PBD into the emissive layer will lead to creation of PBD and PVK exciplex state that will change the dynamics of the system, hence such simple calculation is not necessarily valid. Based on HOMO/LUMO diagram, and very low concentration of **1** in our devices (10% wt) we conclude that it is more likely PVK and PBD exciplex will dominate the dynamics in PLEDs and its contribution in total emission will be greater than 39%.

De-trapping of charges after electrical excitation could also be responsible for the enhanced delayed emission. In this case with PL excitation long lived emission should not be

present, but we observe that it contributes to at least ~36% of the total emission. Consequentially, we assume that the greater part of delayed emission at electrical excitation must come via PBD:PVK exciplex states.

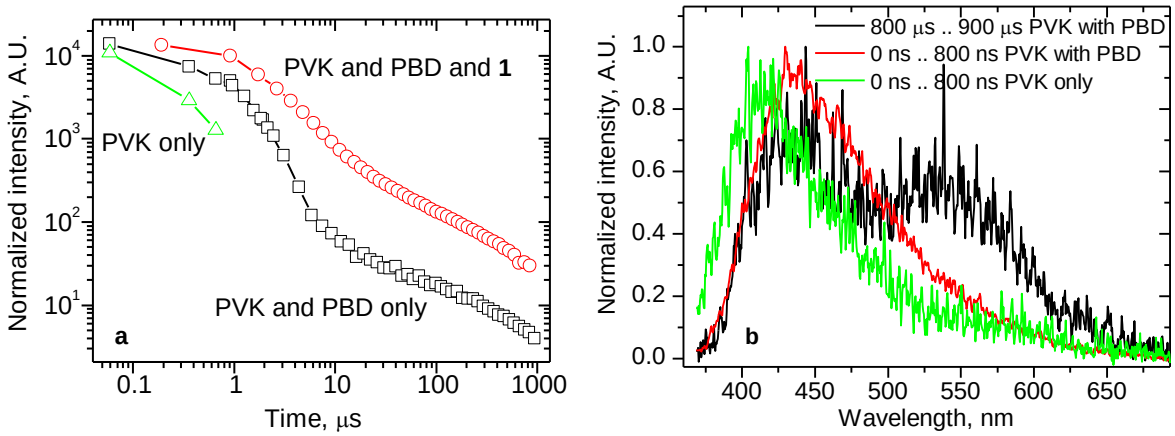

Figure 4. ***a****. EL transients of devices with different active layers. Device with only PVK active layer decays much more rapidly than the ones with PVK:PBD and PVK:PBD:-**1** and it does not have a power law part of decay. The device with PVK and PBD has a shorter exponential part decay component in comparison with PVK:PBD:**1**, and both of them have a power law component indicating that PBD is the origin of this long term decay.* ***b****. Time resolved EL spectra of device with PVK:PBD and PVK only active layers; the former at early (exponential decay region) and late times (power law region).*

This system can be directly compared to that of TPBi-NPB small molecule exciplex devices, as previously described (TPBi is 1,3,5-tris(*N*-phenylbenzimiazole-2-yl)benzene; NPB is *N,N*′-di(1-naphthyl)-*N,N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine). In these devices we confirmed that the bulk of the delayed fluorescence and delayed electroluminescence arises from the p-type delayed emission process, i.e. triplet fusion arising from triplet-triplet annihilation[26], as opposed to the e-type mechanism, i.e. thermally activated delayed fluorescence (TADF)[27]. In this case the NPB $^3\pi$-π^* triplet state is the lowest energy level of the system and through enhanced intersystem crossing (ISC) within the TPBi:NPB exciplex[28] a large triplet population is formed which transfers down to the lowest triplet state of the system, the NPB triplet. Slow triplet migration and subsequent fusion gives rise to a long lived delayed emission (electroluminescence) component. In the case of PVK:PBD:**1**, the Ir complex is the

lowest triplet state of the system and so the exciplex triplet population slowly transfers to the dopant to yield the long-time delayed emission. The long lifetime of the exciplex state reflects the very low/zero mobility of the exciplex excited state and thus the average energy transfer rate to the Ir complex is concomitantly very slow. In both cases the key process is the enhanced triplet formation on the exciplex species. We also note that excimers of the donor also compete with other emissive species in such mixed emitter layers,[29] so it is not surprising that PVK triplet dimers also act as emissive traps as seen here.

4. Conclusions

In conclusion, we show in this communication that PVK and PBD based devices have long lifetime emission lasting up to 1 ms and this emission in some cases can be greater than prompt emission from excitons formed on the dopant initially (up to a few microseconds). The majority of long-lived emission in these devices arises from PVK:PBD exciplex triplet states created during recombination which in turn feed the Ir complex. This long-lived emission from the complex is crucial to the performance of PVK:PBD devices. This exciplex-fed long-lived emission from a heavy metal complex is observed in other PLEDs with PBD (also OXD-7) and PVK doped with blue or green iridium dopants (for details see the supplementary information). It is established, therefore, that this is a general phenomenon rather than one confined to a specific di-iridium case.

Acknowledgments

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[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, Nature 1990, 347, 539.

[2] J. Birks, S. P. McGlynn, *Organic Molecular Photophysics*, Vol. 1, John Wiley & Sons, Bristol 1973.
[3] C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, Journal of Applied Physics 2001, 90, 5048.
[4] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, Journal of the American Chemical Society 2001, 123, 4304.
[5] H. A. Al-Attar, A. P. Monkman, Journal of Applied Physics 2011, 110, 029905
[6] H. A. Al-Attar, G. C. Griffiths, T. N. Moore, M. Tavasli, M. A. Fox, M. R. Bryce, A. P. Monkman, Advanced Functional Materials 2011, 21, 2376.
[7] V. Jankus, A. P. Monkman, Advanced Functional Materials 2011, 21, 3350.
[8] J. Peng, N. Takada, N. Minami, Thin Solid Films 2002, 405, 224.
[9] C. Adachi, T. Tsutsui, S. Saito, Applied Physics Letters 1990, 57, 531.
[10] M. Tavasli, T. N. Moore, Y. Zheng, M. R. Bryce, M. A. Fox, G. C. Griffiths, V. Jankus, H. A. Al-Attar, A. P. Monkman, Journal of Materials Chemistry 2012, 22, 6419.
[11] Y. Zheng,A. S. Batsanov, M. A. Fox,H. A. Al-Attar, K. Abdullah,V. Jankus, M. R. Bryce, A. P. Monkman, Angewandte Chemie, Int. Ed. 2014, 53, 11616.
[12] C. C. Yap, M. Yahaya, M. M. Salleh, Current Applied Physics 2009, 9, 1038.
[13] H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2008.
[14] C. Rothe, S. King, A. P. Monkman, Physical Review B 2006, 73, 245208
[15] C. Rothe, C. J. Chiang, V. Jankus, K. Abdullah, X. S. Zeng, R. Jitchati, A. S. Batsanov, M. R. Bryce, A. P. Monkman, Advanced Functional Materials 2009, 19, 2038.
[16] V. Jankus, C. Winscom, A. P. Monkman, Advanced Functional Materials 2011, 21, 2522.
[17] C. Rothe, A. P. Monkman, Physical Review B 2003, 68, 075208.
[18] V. Jankus, C. Winscom, A. P. Monkman, Journal of Physics-Condensed Matter 2010, 22, 185802.
[19] C. Rothe, S. King, A. P. Monkman, Nature Materials, 2006, 5, 463.
[20] M. Yokoyama, T. Tamamura, M. Atsumi, M. Yoshimura, Y. Shirota, H. Mikawa, Macromolecules 1975, 8, 101.
[21] H. Beens, A. Weller Acta Physica Polonica 1968, 34, 539.
[22] B. Frederichs, H. Staerk, Chemical Physics Letters 2008, 460, 116.
[23] N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Company, Inc, Menlo Park, California 1978.
[24] K. Goushi, K. Yoshida, K. Sato, C. Adachi, Nat Photon 2012, 6, 253.
[25] C. Rothe, S. King, A. P. Monkman, Physical Review Letters, 2006, 97, 076602
[26] V. Jankus, C.-J. Chiang, F. Dias, A. P. Monkman, Advanced Materials, 2013, 25, 1455
[27] F. B. Dias, K. N. Bourdakos, V. Jankus, K. C. Moss, K. T. Kamtekar, V. Bhalla, J. Santos, M. R. Bryce, A. P. Monkman, Advanced Materials, 2013, 25, 3707
[28] S. M. King, R. Matheson, F. B. Dias, A. P. Monkman, J. Phys. Chem. B., 2008, 112, 8010
[29] D. Graves, V. Jankus, F. Dias, A. P. Monkman, Advanced Functional Materials, 2014, 24, 2343.

Supporting Information

The role of exciplex states in phosphorescent OLEDs with poly(vinylcarbazole) (PVK) host

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Complex **2** was synthesized by the literature route;[1] complexes **3** and **4** were obtained from commercial suppliers.

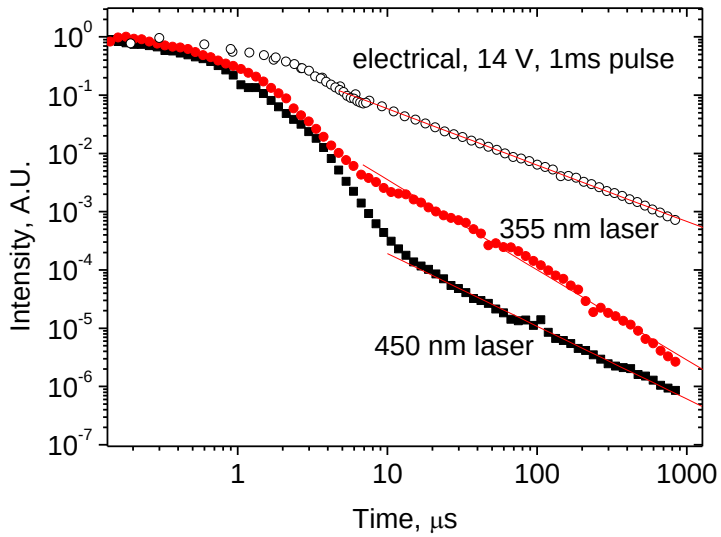

Figure S1. EL (top) and PL (middle and bottom) transients of ITO/PEDOT-PSS/PVK:40% PBD: 5% *fac*-tris(2-phenylpyridine)iridium **3**/Ba/Al devices. Electrical excitation voltage was 14 V and pulse length 1 ms. PL transients were excited at 355 nm (middle curve) and 450 nm (bottom curve). Intensities are normalized.

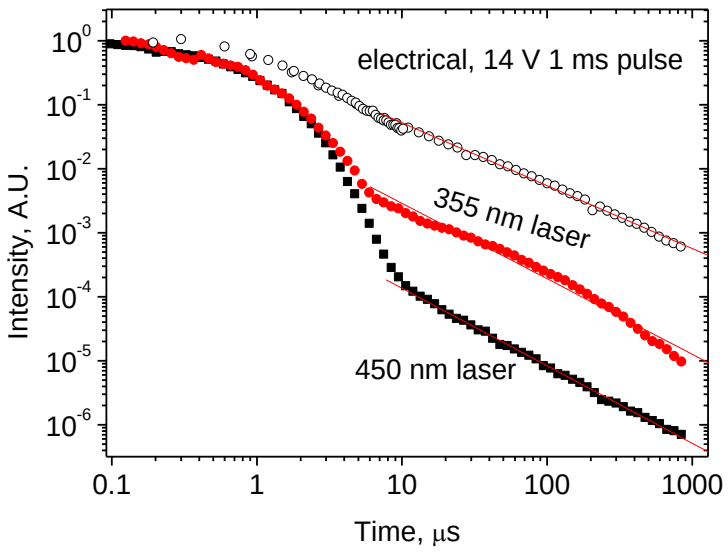

Figure S2. EL (top) and PL (middle and bottom) transients of ITO/PEDOT-PSS/PVK:40% PBD: 5% *fac*-tris[2-(2-pyridinyl-kN)(5-(3,4-bis(2-methylpropyloxy)phenyl) phenyl)-kC]-iridium(III) **4**/Ba/Al devices. Electrical excitation voltage was 14 V and pulse length 1 ms. PL transients were excited at 355 nm (middle curve) and 450 nm (bottom curve). Intensities are offset for clarity.

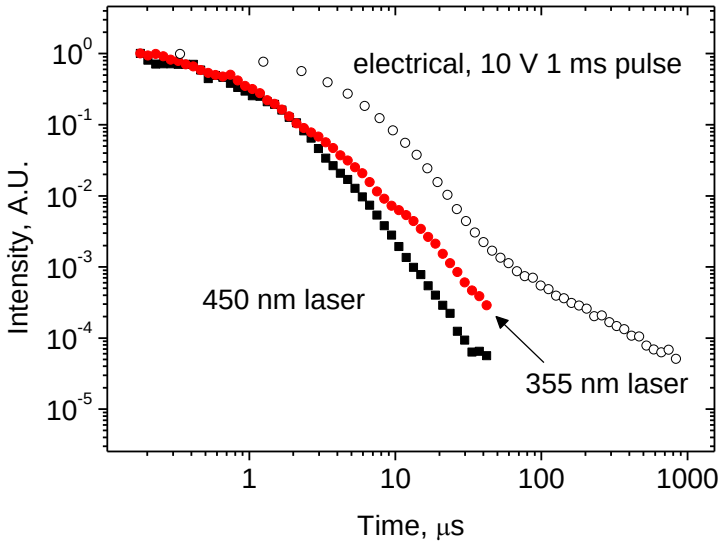

Figure S3. EL (top) and PL (middle and bottom) transients of ITO/PEDOT-PSS/PVK:50% OXD: 8 %(iridium(III)bis[2-(2,4-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato-N,$C^{2'}$]picolinate)-iridium(III) **2**/Ba/Al devices. Electrical excitation voltage was 10 V and pulse length 1 ms. PL transients were excited at 355 nm (middle curve) and 450 nm (bottom curve). Intensities are offset for clarity. Long-lived emission for these devices, with OXD and the blue Ir complex **2**, is less substantial than for the devices with PBD and the green complexes **1**, **3** and **4**; however, it is still present.

References

[1] V. N. Kozhevnikov, Y. Zheng, M. Clough, H. A. Al-Attar, G. C. Griffiths, K. Abdullah, S. Raisys, V. Jankus, M. R. Bryce, A. P. Monkman, *Chem. Mater*. **2013**, *25*, 2352-2358.